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POROUS GLASS CERAMIC BIOIMPLANTS

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A technology for producing porous glass ceramic implants has been developed using foam polyurethane as the burning-out forming matrix. Porous glass ceramics with pore sizes of 300 – 500 and 600 – 700 μm were obtained. Sanitary-chemical, toxicological-hygienic, and medicobiological tests were carried out.

Implants produced from inorganic materials are widely applied in various areas of medicine. Based on their type of behavior in the living organism such implants are classified as inert ones that are morphologically fixed in the organism, resorbable ones that are completely resorbed in the body over time, and bioactive ones that are capable of stimulating osteogenesis and accreting with bone [1]. Moreover, implants can be poreless or can contain pores of various sizes. Porous implants have biological fixation in a living organism as a result of ingrowth in pores of bone and connective tissues. Such implants are used as substitutes for bone tissue fragments in areas of medicine where high strength is not required.

Crystalline glass or glass ceramic materials are promising for medical applications. These materials are biologically active and are distinguished by a diversity of compositions and properties and the possibility of purposefully controlling their phase compositions.

Of special interest are porous glass ceramic implants suitable as substitutes for bone tissue fragments. They provide for strong fixation of the implant to the bone, while the biological activity of the implant precludes its rejection.

Thus, implants with bioactive and biological methods of fixation in a living organism are promising for medical use. The combining of these two methods, which is accomplished by the creation of porous bioactive materials, makes it possible to reliably fix the implant without harming the living organism.

For a number of years Belarus State Technological University has been developing glass ceramic bioimplants based on the $K_2O - CaO - P_2O_5 - Al_2O_3 - SiO_2 - F$ system, in which the main crystalline phases were tricalcium phosphate $Ca_3(PO_4)_2$ and fluorapatite $Ca_5F(PO_4)_3$. The implants obtained were intended for filling bone defects in maxillofacial surgery (removal of cysts, paradontosis, etc.). The most suitable variant of use of the developed glass ceramic material is in the form of granules with a grain size of 300 – 500 μm. A glass ceramic granulated material based on Biositall-11 successfully passed one-year clinical tests at four Belarus clinics, and the Ministry of Health of Belarus issued an authorization for its clinical use.

At present, Biositall-11 granules are produced at an experimental production facility of Belarus State Technological University and are supplied to dental clinics.

Long-term use of these granules revealed certain features of their behavior in the body. In the first stages, the process of osteogenesis is very active, the granules are enveloped by connective and newly formed bone tissue, and partial intergrowth of bone tissue between the granules takes place. However, complete resorption of the granules does not take place, since the diffusion processes gradually become retarded.

The granulated material can be used only for filling slight bone defects. It is not suitable as a filler for large bone defects. Therefore, the problem of imparting specific shapes to implants and making them thin-walled arose.

The creation of porous glass ceramics with a controlled pore size was found to be most suitable. It was established that the pore size in such materials should exceed 100 μm, since only in this case will bone and connective tissues growing into the pores be viable [1].

Since porous glass ceramics can be produced only by sintering the initial devitrified glasses, it was necessary to develop a new glass ceramic composition, since Biositall-11 is not sinterable due to the substantial amount of crystalline phases forming under heat treatment. A new glass ceramic composition was developed on the basis of the same system as Biositall-11, but it yielded a somewhat smaller amount of the crystalline phase that forms under heat treatment.

The most complicated problem was the development of a technology for producing a porous structure with a controllable pore size. The specific method for producing the porous material was determined by the set of properties imposed on

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the material, including the required porosity and pore size and geometrical parameters.

Our aim was to produce a porous glass ceramic material with a pore size of 300 – 700 μm, since, according to some researchers, the optimum pore size in providing for osteogenesis and bone intergrowth in pores is around 500 μm.

Based on an experimental analysis of different methods for producing porous structures, we selected a method is which a cellular polymer is the forming element. This method is a variation of the burning-out additive method and is used in the production of highly porous permeable cellular materials that are characterized by a well-developed specific surface and a low bulk density [2, 3].

An advantage of the selected technology consists in the fact that the structure of the pore space of the developed material is closely related and virtually identical to the structure of the cellular organic polymer used in the process. This means that in the stage of controlling the structure of the polymer used, it is possible to predict the porous structure and the pore size of the end material. The selected technology is simple and economical, and under the corresponding technological conditions it makes it possible to provide the required phase composition of the bioimplant.

The technology for the production of porous glass ceramics consists of the following stages: glass synthesis, glass milling; preparation of the glass slip; impregnation of the cellular polymer with the required pore size with the slip; removal of excessive slip; drying of the intermediate product; heat treatment of the intermediate product in accordance with a strictly prescribed procedure.

Studies of the effect of technological factors on the chemical and mechanical properties of porous implants and preliminary sanitary-chemical and medicobiological tests established that the composition of the glass matrix, which is the structural basis for the porous glass ceramics, has a substantial effect on the chemical solubility of the material due to its well-developed surface. In this context, the glass compositions were adjusted in order to decrease or completely eliminate components that are unfavorable from the sanitary-chemical aspect. The glasses virtually should not contain aluminum and magnesium oxides, which were subsequently washed out in model acid media, and their concentration in the solutions exceeded the maximum permissible concentration. These results were taken into account in the development of the glass composition for a porous bioimplant. The molar content of magnesium oxide in the optimum glass composition 7.1 was decreased to 0.5%, and aluminum oxide was completely eliminated. At the same time, the correction to the composition did not affect the composition of the crystalline phases formed under heat treatment (fluorapatite and tricalcium phosphate) or the biological properties of the glass ceramics.

The phase composition of a glass ceramic material based on glass 7.1 is shown in Fig. 1. It is generally known that calcium phosphates are desirable crystalline phases in implant

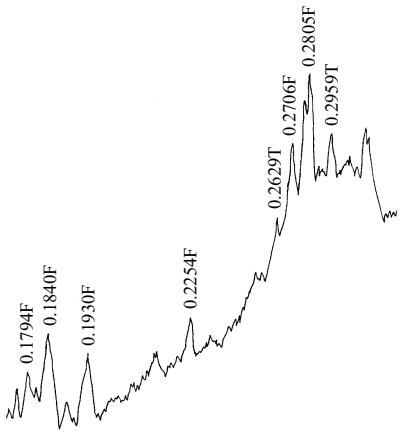

Fig. 1. X-ray pattern of glass ceramic 7.1: F) fluorapatite $Ca_5F(PO_4)_3$; T) tricalcium phosphate $Ca_3(PO_4)_2$.

materials, since they significantly increase their biological activity. As a result of complex physicochemical and biochemical reactions between bone and the bioglass ceramics, the latter are able to stimulate the osteogenesis process and grow into the bone.

Glass of composition 7.1 was melted in a gas-flame furnace at a temperature of 1500 – 1550°C and was cast into water to obtain granules. The granules were then milled in a ball mill of the Sand type to a particle size of 5 – 10 μm. The prepared suspension consisted of glass powder, 40 – 50% water, and plastifier additives. A cellular polymer whose pore size and structure were selected based on the desired pore size and structure of the end glass ceramic material was impregnated with this suspension. After drying at a temperature of 230 – 240°C, the intermediate products underwent heat treatment that includes burning out of the organic substrate, devitrification, and sintering.

The physicochemical properties of the porous material depend not only on the composition of the slip used but also on the time/temperature conditions of the heat treatment. The latter should be such that loss of shape of the cellular skeleton is prevented in the course of sintering. It is characteristic that the strength parameters of the porous glass ceramics depend on the end temperature of the material sintering. When the sintering temperature exceeded the optimum value, the material became so strong that it could not be processed mechanically by medical instruments. This is completely undesirable, since an implant should easily acquire the required shape under mechanical treatment.

As a result of heat treatment in accordance with the optimum technological conditions, white-colored porous glass ceramics were obtained with an average pore size of 300 – 500 and 600 – 700 μm, depending on the type of cellular polymer used. The structure of a porous glass ceramic material based on glass 7.l is shown in Fig. 2. The microphotographs of the surface and a fracture of the material clearly exhibit a uniform porous structure. At × 100 magnification, the glass ceramic structure of the walls between the pores be-

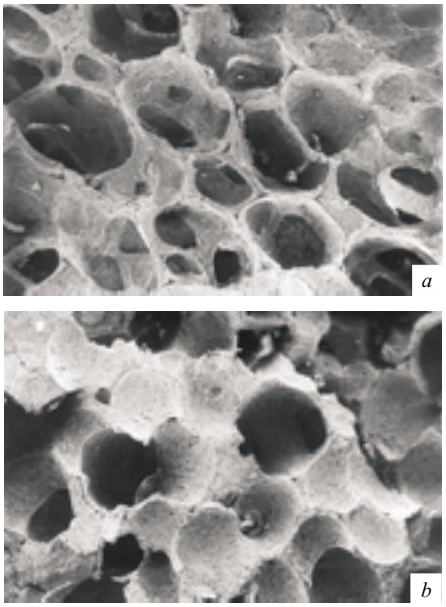

Fig. 2. Microphotographs (× 30) of the structure of porous glass ceramics IPS-7.1: surface (*a*) and fracture (*b*).

comes clearly visible. The pores are mostly communicating, channel-shaped, and rounded, which creates favorable conditions for active penetration of bone and connective tissues of the living organism in them. The porosity of the material is 50 – 70%.

Medicobiological studies of the glass ceramics obtained demonstrated that coalescence of the material proceeded without clinical complications. Active hystological regeneration of the tissues adjacent to the implanted material developed on the 7th day. After 14 days, regenerated bone material formed around the glass ceramic implant, and formation of bone trabeculae was registered. Directed growth of these trabeculae into edge portions of the bioglass ceramic pores was observed.

Twenty-one days after the implantation, no inflammatory phenomena were observed. The implant is macroscopically well fixed by compact tissue in edge portions of the defect. The connective tissue is represented by a large number of vessels and fibroblast cells. Soft and bone tissues growing into implant pores are clearly registered, which is evidence of good compatibility of the bioceramic material with tissues of the living body.

Sanitary-chemical and toxicological-hygienic tests were conducted as well. Porous glass ceramic material IPS-7.1 is recommended for clinical tests.

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